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Spectroscopic evidence for a surface layer in CuInSe_2 :Cu deficiency

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The near-surface region of thin-film polycrystalline (PX) $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) is considered important because it is the region where the electrical junction forms in a CIGS photovoltaic device. Spectroscopic ellipsometry measurements of polycrystalline CuInSe_2 films reveal that there is a thin layer at the surface which has different optical and electronic properties from those of the bulk film. This surface layer of thin-film CIGS has a larger band gap and greater spin-orbit interaction energy than the bulk film. These properties indicate that the surface layer is more Cu deficient than the bulk in the nearly stoichiometric thin-film PX-CIGS used in photovoltaic devices. This work provides an insight into the importance of surface layer engineering for photovoltaic device design. © 2007 American Institute of Physics. [DOI: 10.1063/1.2755718]

Single-wavelength ellipsometry has historically been used for measuring the thickness of a film. Spectroscopic ellipsometry has been used for determining both film thickness and the optical properties of materials. Historically, researchers faced a problem in accounting for surface roughness in analysis of ellipsometric data. Aspnes and Theeten modeled the dielectric effects of microscopic roughness at the surface using an effective medium approximation (EMA).¹ Their approach mathematically models the dielectric effect of surface roughness by introducing a thin surface layer composed of a 50%-50% EMA mixture of the optical properties of the underlying bulk material with the optical properties of void. This technique has become a recognized standard for obtaining accurate optical properties of the bulk material in spite of the difficulties associated with nonideal surfaces. In this study, we take the technique of Aspnes and Theeten one step further by allowing the optical properties of the nonvoid component of the surface layer EMA to vary independent of the underlying bulk optical constants. The validity of our technique is verified by the factor of 2 improvement in the quality of fit to the ellipsometry data. This enables a method for investigating the optical properties and electronic structure of the surface layer.

Thin-film chalcopyrite polycrystalline (PX) $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) is used as the absorber layer for high efficiency photovoltaic solar cells. The efficiency of laboratory thin-film PX-CIGS solar cells has surpassed 19%.² The total area conversion efficiency for $\text{ZnO}/\text{CdS}/\text{CuInSe}_2$ (CIS) solar cell has been up to 14.5%.³ High efficiency solar cells always use slightly Cu-poor (23.5–24.5 at. % Cu) PX $\text{CuIn}_{0.72}\text{Ga}_{0.28}\text{Se}_2$. The surface layer of CIS/CIGS is considered important because it is the region where the electrical junction forms in photovoltaic devices and it plays a crucial role in the device performance.⁴ There have been studies on junction formation between PX-CdS and CIS/CIGS thin

films, as is the standard in CIS/CIGS photovoltaic devices.⁵ Schmid *et al.*⁶ suggested a model for the formation of a chalcopyrite/ordered vacancy compound *p-n* heterojunction in PX-CIS. Jiang *et al.*⁷ measured the built-in electrical potential of CIGS using scanning Kelvin probe microscopy. They suggested that the *p-n* junction is a buried homojunction located in the CIGS film, 30–80 nm from the CIGS/CdS interface.

There have been numerous studies on the properties of the surface of CIS/CIGS materials. Yan *et al.*⁸ found that the surface region and the bulk of CIGS are structurally similar, with no ordered defect chalcopyrite structure observed, but the chemical composition of the surface is slightly different than the composition of the bulk. Romero *et al.*⁹ reported that the surface of thin CIGS films has wider band gap than the bulk. An angle resolved x-ray photoelectron spectroscopy study on epitaxial thin CIS films showed that a severe Cu depletion exists on the top of one to two layers.¹⁰ Energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy studies on thin-film PX-CIS showed that CIS layers have a Cu-deficient surface composition.⁵ Grazing incidence x-ray diffraction analysis by Kötschau and Schock¹¹ showed that there exists a Cu-depleted surface layer in thin CIS films, which is expected to be due to the reconstruction of the surface of slightly Cu-deficient CIS film. Another grazing incidence x-ray diffraction analysis by Hasoon *et al.*¹² revealed a small shift toward higher angles as the angle of incidence decreases for the (220/204) peaks, which can be an evidence for a Cu-depleted surface.

The spectroscopic ellipsometer used in this study is a J. A. Woollam M2000 variable angle spectroscopic ellipsometer that adopts a rotating compensator design. For this study, we used angles of incidence at $\varphi_a=65^\circ$, 70° , 75° , and 80° to ensure an accurate determination of the parameters used in the model. We prepared slightly Cu-poor thin-film PX-CIS (21.6 at. % Cu) (Ref. 13) to compare the optical properties and electronic structure of a bulk layer in this film with those of a surface layer in nearly stoichiometric thin-film (α -phase) PX-CIS (24.1 at. % Cu). Our results will apply equally well

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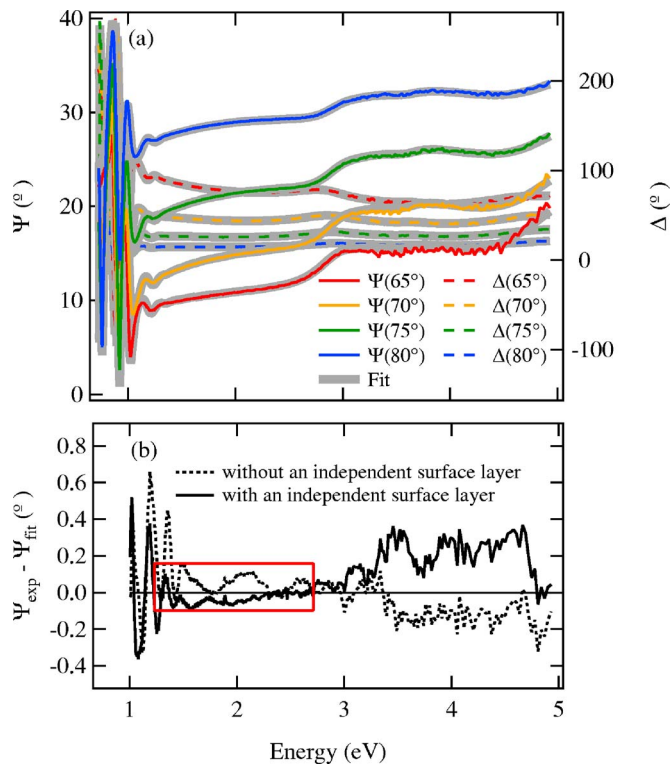


FIG. 1. (Color online) (a) Fit results of Ψ and Δ in 0.7–5.0 eV. Experimental Ψ and Δ are depicted as thinner color solid and dashed lines. From the top in the spectral region of 4–5 eV, they are $\Psi(80^\circ)$, $\Psi(75^\circ)$, $\Psi(70^\circ)$, $\Psi(65^\circ)$, $\Delta(65^\circ)$, $\Delta(70^\circ)$, $\Delta(75^\circ)$, and $\Delta(80^\circ)$. Calculated Ψ and Δ are depicted as thicker gray lines. (b) Difference in Ψ between the data and the fit with and without an independent surface layer dielectric function at the incidence angle of 75° in 0.7–5.0 eV.

to CIGS since the replacement of In with Ga is an isoelectronic substitution that does not significantly alter the effects of Cu deficiency in terms of electronic structure. The thin CIS film layer is deposited onto molybdenum-coated soda-lime glass. A schematic diagram of the mathematical model used in data analysis can be found elsewhere.^{13,14} Samples are prepared with the same structure used in an actual PX photovoltaic device with the exception of the lack of the CdS window layer and the ZnO conducting transparent oxide. Thicknesses of the molybdenum and CIS films are approximately 1.0 and 1.3 μm , respectively. These films are grown by a single-stage coevaporation technique that provides homogeneous films except for the Cu-poor surface region, which exists for the 60 nm from the top of the film surface. This thickness has been determined from Auger electron spectroscopy depth profiling. In this deposition technique, the fluxes of the copper, indium, and selenium were kept constant during deposition.

Figure 1(a) shows the fit results of Ψ and Δ at the incidence angles of $\varphi_a=65^\circ$, 70° , 75° , and 80° in the spectral region of 0.7–5.0 eV for nearly stoichiometric thin-film PX-CIS. We find that the value of mean squared error¹⁵ in the spectral range of 0.7–5.0 eV is improved from 8.3 to 3.6 by replacing the standard surface layer (depending on a underlying bulk layer optical constant) with a surface layer independent of the bulk optical constants.¹⁶ Figure 1(b) shows the difference between the calculated fit and the experimental data in the Ψ spectrum at $\varphi_a=75^\circ$. The fit is significantly improved in the fundamental band gap region, as shown in Fig. 1(b), with a guidance box when an independent surface

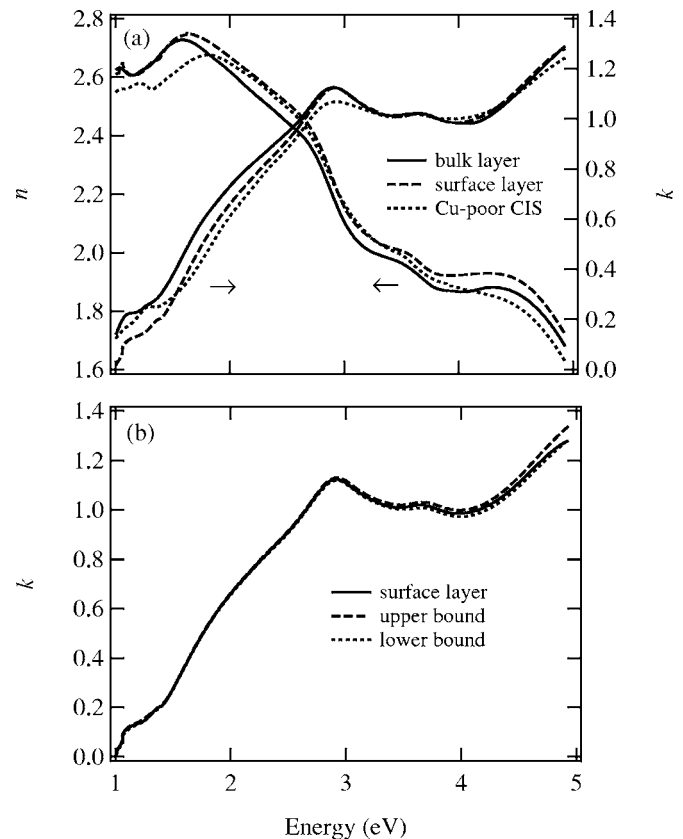


FIG. 2. (a) Optical constants n and k of a bulk layer, a surface layer, and a Cu-poor CIS with 21.6 at. % Cu. (b) Extinction coefficient k of a surface layer with its upper and lower bounds.

layer is used in the surface layer compared with the previous work,¹⁶ where we used effective medium approximation with the underlying CIS layer with void. Standard deviation is also decreased from 0.13 to 0.09. Without an independent surface layer, the fit was satisfactory; however, with that, the difference between calculated fits and experimental data is reduced to even within a resolution in Ψ ($\sim 0.1^\circ$) in a fundamental band gap region. Light starts to be absorbed from the band gap (~ 1 eV) and due to transparency caused by low absorption below the band gap, ellipsometric parameters Ψ and Δ stay oscillatory with decreasing amplitude until there is no more back reflection in the sample.

Figure 2(a) compares three optical functions. The thick and thin solid lines represent the optical functions of the bulk layer and surface layers in the nearly stoichiometric thin-film PX-CIS, respectively, and the dashed line represents the bulk layer in the slightly Cu-poor thin-film PX-CIS.¹⁶ Figure 2(b) presents the extinction coefficient (solid line) with upper (dashed line) and lower (dotted line) bounds for the purpose of indicating the uncertainty in the amplitude of k . We determined the lower and upper bounds of k by calculating the model dielectric function of the surface layer by inserting the lower and upper values of the amplitude of each oscillator function. It is crucial to have an accurate determination of the amplitude of the extinction coefficient in the 1–3 eV range since this spectral range is particularly suggestive of the degree of Cu deficiency in CIS due to reduced p - d repulsion caused by the removal of Cu $3d$ hole density of state at the valence band maximum.^{14,16,17} This weakens the optical transition $E_0(A, B, C)$ along Γ line in k space.¹⁴ A more thorough description of the optical transition in 1–5 eV is dis-

TABLE I. Critical points analyzed by the model dielectric function method.

Critical points	Bulk layer	Surface layer	Cu-poor CIS ^a
$E_0(A, B)$	1.026	1.052	1.080
$E_0(C)$	1.220	1.250	1.290
Δ_{so}	0.194	0.198	0.210

^a21.6 at. % Cu.

cussed in detail elsewhere.^{14,18} Based on the fact that the uncertainties start to be substantial above $E \sim 3$ eV, they are expected to be caused by the polycrystallinity in PX-CIS since the grain size is comparable to the wavelength of the light source in 3–5 eV.¹⁴

There is a similarity between the optical functions of the surface layer of nearly stoichiometric thin-film PX-CIS and the bulk layer of slightly Cu-poor thin-film PX-CIS. In particular, both materials exhibit a reduction in the extinction coefficient k in 1–3 eV relative to that for nearly stoichiometric PX-CIGS. This has been shown to be a clear indicator of Cu deficiency.¹⁶ Depression of the extinction coefficient k of Cu-poor PX-CIGS is observed in the 1–3 eV spectral range due to a reduction in repulsive interaction between Cu 3d and Se 4p states caused by Cu deficiency at the valence band maximum, which is consistent with our previous work¹⁶ and the theoretical calculations by Persson and Zunger.¹⁷ This implies that Cu is more deficient at surface region than in the bulk region of thin CIS films.

The optical properties of the surface layer for the nearly stoichiometric thin-film PX-CIS in Fig. 2(a) suggest that the reduction in the extinction coefficient is greater than expected in the 1.0–1.5 eV range compared with the reduction in the extinction coefficient for slightly Cu-poor thin-film PX-CIS since lower extinction coefficient k is observed for the surface layer of the CIS with 24.1 at. % Cu than for the bulk layer of the CIS with 21.6 at. % Cu. That is, Cu deficiency is greater at the surface layer of nearly stoichiometric thin-film PX-CIS than at the bulk layer of Cu-poor thin-film PX-CIS, contrary to the trend in 1.5–3.0 eV. This is also confirmed by the critical point energy analysis,^{16,18} as shown in Table I. The band gap E_g , determined by the smallest critical point energy $E_0(A, B)$, and spin-orbit interaction energy $\Delta_{so} (=E_0(C) - E_0(A, B))$ (Ref. 16)) of the surface layer are greater than that of the bulk layer but less than that of Cu-poor CIS (see Table I). The analysis method of the critical points and the definition of E_0 transition can be found elsewhere.^{14,18}

The increase of the band gap for Cu-poor CIS can be explained in terms of electronic structure near the valence band maximum. Less p - d repulsion in slightly Cu-poor thin-film PX-CIS than in nearly stoichiometric thin-film PX-CIS results in a lowering of the valence band maximum. Hence the increase of the band gap is expected from nearly stoichiometric thin-film PX-CIS to slightly Cu-poor thin-film PX-CIS.¹⁶ The increase of spin-orbit interaction is found, which is also an indication of Cu deficiency at a surface layer. The spin-orbit splitting (Δ_{so}) of the uppermost valence band observed in the ternary compounds is composed of two atomic components Δ_p and Δ_d in such a way that the negative atomic Δ_d of the Cu 3d levels partially cancels out the positive atomic Δ_p of Se 4p levels. The amount of hybridization can be expressed quantitatively by¹⁹

$$\Delta_{so} = \alpha\Delta_p + (1 - \alpha)\Delta_d, \quad (1)$$

where Δ_p is the spin-orbit splitting observed in the p -like binary analogue, Δ_d is that observed in Cu d levels, and α is the fractional p -like character of the uppermost valence bands. So in the case of stoichiometric CIS,¹⁹ $\alpha = \frac{2}{3}$, but for Cu-poor CIS,¹⁹ $\alpha > \frac{2}{3}$. Thus the value of Δ_{so} increases when Cu gets more deficient. From larger values of band gap and spin-orbit interaction energy at the surface layer, we can conclude that the at. % of Cu of the surface layer is less than 24.1 at. %.

In summary, we provide spectroscopic evidence for Cu deficiency in the surface layer of the nearly stoichiometric thin-film PX-CIS. The reduction in absorption in the spectral region of 1–3 eV and the increase in the band gap at the surface layer are found for nearly stoichiometric thin-film PX-CIS. We find that the surface layer is more Cu deficient than a bulk layer in the nearly stoichiometric thin-film PX-CIS. This work presents the possibility of probing the optical and electronic properties of a surface layer in the thin-film polycrystalline semiconductors by adopting a material layer with voids using effective medium. This work is also of significance in engineering of the solid-state electronic and optoelectronic device design near the junction interface.

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¹D. E. Aspnes and J. B. Theeten, Phys. Rev. B **20**, 3292 (1979).²K. Ramanathan, M. A. Contreras, C. L. Perkins, S. Asher, F. S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, and A. Duda, Prog. Photovoltaics **11**, 225 (2003).³J. A. M. Abushama, S. Johnston, T. Moriarty, G. Teeter, K. Ramanathan, and R. Noufi, Prog. Photovoltaics **12**, 39 (2003).⁴A. Niemegeers, M. Burgelman, R. Herberholz, U. Rau, D. Hariskos, and H.-W. Schock, Prog. Photovoltaics **6**, 407 (1998).⁵R. Herberholz, U. Rau, H. W. Schock, T. Haalboom, T. Gödecke, F. Ernst, C. Beilharz, K. W. Benz, and D. Cahen, Eur. Phys. J.: Appl. Phys. **6**, 131 (1999).⁶D. Schmid, M. Ruckh, F. Grunwald, and H. W. Schock, J. Appl. Phys. **73**, 2902 (1993).⁷C.-S. Jiang, F. S. Hasoon, H. R. Moutinho, H. A. Al-Thani, M. J. Romero, and M. M. Al-Jassim, Appl. Phys. Lett. **82**, 127 (2003).⁸Y. Yan, K. M. Jones, J. Abushama, M. Young, S. Asher, M. M. Al-Jassim, and R. Noufi, Appl. Phys. Lett. **81**, 1008 (2002).⁹M. J. Romero, K. M. Jones, J. Abushama, Y. Yan, M. M. Al-Jassim, and R. Noufi, Appl. Phys. Lett. **83**, 4731 (2003).¹⁰D. Liao and A. Rockett, Appl. Phys. Lett. **82**, 2829 (2003).¹¹I. M. Kötschau and H. W. Schock, J. Phys. Chem. Solids **64**, 1559 (2003).¹²F. S. Hasoon, Y. Yan, H. Althani, K. M. Jones, H. R. Moutinho, J. Alleman, M. M. Al-Jassim, and R. Noufi, Thin Solid Films **387**, 1 (2001).¹³S.-H. Han, F. S. Hasoon, H. A. Al-Thani, A. M. Hermann, and D. H. Levi, Appl. Phys. Lett. **86**, 021903 (2005).¹⁴S.-H. Han, C. Persson, F. S. Hasoon, H. A. Al-Thani, A. M. Hermann, and D. H. Levi, Phys. Rev. B **74**, 085212 (2006).¹⁵H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry: A User's Guide*, 1st ed. (Wiley, New York, 1999), p. 101.¹⁶S.-H. Han, A. M. Hermann, F. S. Hasoon, H. A. Al-Thani, and D. H. Levi, Appl. Phys. Lett. **85**, 576 (2004).¹⁷C. Persson and A. Zunger, Phys. Rev. Lett. **91**, 266401 (2003).¹⁸M. I. Alonso, K. Wakita, J. Pascual, M. Garriga, and N. Yamamoto, Phys. Rev. B **63**, 075203 (2001).¹⁹J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, 1st ed. (Pergamon, Oxford, 1975).